FINAL REPORT

on the study of

REACTION KINETICS OF ACCELERATING FLAMES

supported by

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I. OBJECTIVE

The research program was concerned essentially with a study of the relationship between the kinetics of chemical reactions associated with a high rate of energy release, and the gas dynamics of wave phenomena which, as a rule, accompany such processes. The ultimate purpose of the investigation was to settle the fundamental problem concerning the relative influence of the reaction rate and transport phenomena on the generation of pressure waves by the process of chemical energy release in gaseous mixtures.

II. ACCOMPLISHMENTS

The principal feature of the method of attack was to restrict the scope of inquiry with respect to chemistry by the primary use of the ozone decomposition reaction.

In order to accomplish such an objective an ozone production plant was built. It was based on the use of a Welsbach T-23 laboratory ozonator where a moderately low concentration ($\sim$ 5 w/o) of ozone was at first obtained in pure oxygen by the action of corona discharge. The mixture was passed then to an ozone concentrator where it was cooled down in a liquid oxygen bath. The excess oxygen was subsequently distilled off as the pressure was decreased to approximately 1 mm Hg by a mechanical vacuum pump, reducing the oxygen content to almost 1 pro-mille in mole fraction. The ozone was then evaporated and stored under atmospheric pressure and room temperature in a stainless steel vessel of 500 in^3 capacity. With exception of the liquid oxygen Dewar flask and the "cold finger" where the mixture was condensed, the whole apparatus was made out of stainless steel. It was housed in an enclosure of 1/4" aluminum plate shields, and all operations were performed by remote control.

Most of the experiments were carried out with the use of Pyrex glass tubes of inside diameters of 1 in., 1/2 in., 1/4 in., and 1 mm. The 1/2 in. and 1/4 in. tubes were made up of five carefully aligned 6 ft. sections connected into a 30 ft. total length by flanges and Neoprene O-rings. For the experiments in the 1 in. diameter tube its 30 ft. long section was connected to a similarly long section of the 1/2 in. tube yielding a tube length of 63 ft. which permitted the achievement of a fully developed detonation wave. The 1 mm tube consisted of two sections: 18 ft. of the 1/4 in. tube at the ignition end and 15 ft. of fused 30 in. pieces of precision-bore ($\pm$ 0.0003 in.) 1 mm tube. All tubes were covered with heavy black tape to keep stray light out, and were mounted on a metal frame.

Ignition either by spark or glow-coil was always performed at one end, while observations of the waves were made by means of a system of four optically aligned RCA 1P21 photomultiplier sensors near the other end. The signals from the photomultipliers were converted through thyratron circuits into shaped pulses and superimposed upon a raster oscilloscope sweep. In this way the wave propagation velocity could be measured with an uncertainty of less than 0.2%.

Besides the work with the ozone-oxygen system, studies were also conducted, with a partial support of the NASA Grant, on the generation of pressure waves by accelerating flames in hydrogen-oxygen mixtures. On one hand, this provided much easier means for the gasdynamic experiments, but, on the other, the kinetics in this case were too involved to yield satisfactory information on the relationship between the dynamic and chemico-kinetic processes that represented the major objective of the program.

The results of the study can be summarized as follows:

While the experimental observation of wave processes and their gasdynamic interpretation were quite fruitful, the establishment of a link between the fluid dynamic effects and the kinetics was seriously handicapped by the lack of information on the reaction mechanism at the high temperature level of the accelerating flame and detonation.

In particular it was found that the known "low temperature" kinetics of the ozone decomposition reaction scheme, which seemed quite reliable up to about 1000 ^{o}K, could not be extrapolated with the use of the same rate expressions to the 3000 ^{o}K level of the detonation wave. It became necessary therefore to concentrate first on the observation of the structure of the fully developed detonation, where the kinetic effects should be predominant, before attempting to study the process of flame acceleration for which the knowledge of kinetics is a necessary prerequisite. In the meantime it was also established that even the existing knowledge of detonation velocities in ozone-oxygen mixtures was not accurate enough for the purpose of this study, while, at the same time, recent advances in the theory of vibrational relaxations suggested that exact measurement of this parameter may be of particular significance in this respect as well.

Consequently, after some preliminary observations of the development of detonation in ozone-oxygen mixtures, the program of research was modified in order to improve first the knowledge on the characteristics of the steady detonation wave and on the corresponding "high temperature" kinetics which could not be treated in a satisfactory manner by the classical theory.

As a result of the experimental program the velocity of steady detonation waves in gaseous ozone have been measured over a wide range of conditions: in tubes of diameter between 1 and 25.4 mm, at initial pressures between 80 and 220 mm Hg and in mixtures containing from 72.5 to 96.6% ozone in oxygen, argon and helium. The results, extrapolated to infinite tube diameter, agree, within the experimental error, with the calculated Chapman-Jouguet detonation velocities corresponding to complete thermodynamic equilibrium of reaction products.

The results of the analytical work that was carried out at the same time have been quite revealing. The computations of isothermal reaction processes demonstrated the inadequacy of the quasi-steady state approximation. This led to their refinement by the use of a singular perturbation technique that has been developed recently for the study of boundary layer phenomena.

Furthermore, exact determinations of Hugoniot curves and Chapman-Jouguet states have been made by means of an IBM 7040 computer with the use of the best available thermodynamic equilibrium data. The structure of the detonation wave has been determined by a numerical analysis that took into account the effect of transport phenomena with chemical kinetics described in terms of the quasi-steady-state approximation. A program for the computation of wave structure, taking into account the whole chain-kinetic scheme of the reaction, but without consideration of transport processes (the von Neumann-Döring-Zeldovich model) has been also worked out.

In March 1963 a proposal (UCBSSL 154) was submitted to NASA for support of the continuation of this program of research. Unfortunately it was not granted. Consequently the work had to be terminated before any insight into the wave structure could be gained. This was particularly regrettable in view of the fact that both the experimental and analytical results gave clear indication of the significance that such experiments could yield in clarifying the relationship between reaction kinetics and the gasdynamic effects of wave processes.

III. PUBLICATIONS

Major achievements of the study have been described in the following publications:

1. "Study of Detonation in Ozone-Oxygen Mixtures", by J. R. Bowen and A. K. Oppenheim, University of California Report, October, 1962.

2. "Contributions to the Theory of the Structure of Gaseous Detonation Waves", by D. B. Spalding, IXth Symposium (International) on Combustion, pp. 417-423, Academic Press, New York, 1963.

3. "Determination of the Detonation Wave Structure", by A. K. Oppenheim and J. Rosciszewski, IXth Symposium (International) on Combustion, pp. 424-441, Academic Press, New York, 1963.

4. "Singular Perturbation Refinement to Quasi-Steady State Approximation in Chemical Kinetics", by J. R. Bowen, A. Acrivos, and A. K. Oppenheim, Chemical Engineering Science, 18, pp. 177-188, 1963.

5. "A Study of Detonation Velocities in Gaseous Ozone", by R. W. Getzinger, J. Ray Bowen, A. K. Oppenheim, and M. Boudart, University of California Technical Note enclosed as appendix.

6. "Steady Detonations in Gaseous Ozone", (Project Squid Technical Report UCB-3-P, University of California, May 1964, 37 pages) presented at the X Symposium (International) on Combustion, Cambridge, England, August 17-21, 1964. (to be published in the Proceedings).

Also partially supported by the Grant, and containing acknowledgment to this effect, are the following papers:

1. "Development and Structure of Plane Detonation Waves", by A. K. Oppenheim, Fourth AGARD Symposium on Combustion and Propulsion, pp. 186-258, Pergamon Press, 1961.

2. "Influence of Wave Reflections on the Development of Detonation", by A. J. Laderman and A. K. Oppenheim, Physics of Fluids, 4, 778-782, 1961.

3. "Measurement of Pressure Field Generated at the Initiation of Explosion", by A. J. Laderman, P. A. Urtiew and A. K. Oppenheim, Proceedings of the ASME Symposium on Measurement in Unsteady Flow, 32-35, 1962.

4. "Initial Flame Acceleration in an Explosive Gas", by A. J. Laderman and A. K. Oppenheim, Proceedings of the Royal Society, A268, 153-180, July, 1962.

5. "On the Generation of a Shock Wave by Flame in an Explosive Gas", by A. J. Laderman, P. A. Urtiew and A. K. Oppenheim, Proceedings of IX Symposium (International) on Combustion, 265-274, Academic Press, New York, 1963.

6. "The Onset of Retonation", by A. K. Oppenheim, A. J. Laderman and P. A. Urtiew, Combustion and Flame, 6, 3, 193-197, September, 1962.

7. "Effect of Ignition Geometry on Initial Flame Acceleration in a Spark Ignited Explosive Gas", by A. J. Laderman, P. A. Urtiew and A. K. Oppenheim, Combustion and Flame, 6, 4, 325-335, December, 1962.

8. "Recent Progress in Detonation Research, by A. K. Oppenheim, N. Manson and H. Gg. Wagner, AIAA Journal, 1, 10, 2243-2252, October, 1963.

9. "Significance of Detonation Study to Propulsion Dynamics", by A.K. Oppenheim and A. J. Laderman, Proceedings of the 14th IAF Congress, Paris, France, September 25-October 1, 1963.

10. "Gasdynamics Effects of Shock-Flame Interactions in an Explosive Gas", by A. J. Laderman, P. A. Urtiew and A. K. Oppenheim, presented at the 1964 Summer Meeting of the AIAA (submitted for publication).